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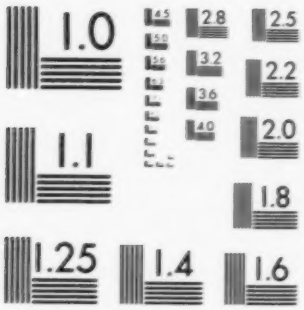

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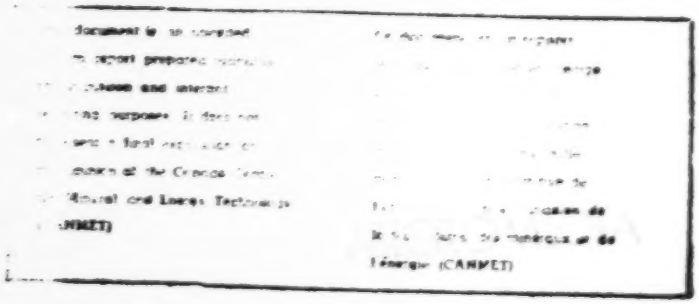
CORROSION STUDIES IN SIMULATED FLUIDIZED BED COAL COMBUSTION ENVIRONMENTS. PART I - SCALING BEHAVIOUR

A.W. Lui, V.E. Moore and J.T. McGoey

Corrosion Science and Engineering & Metal Physics Sections

July 1982



Energy Research Program

22 pp

PHYSICAL METALLURGY RESEARCH LABORATORIES

REPORT: ERP/PMRL 82-49(TR)

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A.W. Lui*, V.E. Moore** and J.T. McGoey***

ABSTRACT

Four stainless steels (types 304, 316, 310 and Uddeholm 904L) and four experimental alloys (Fe-8.4 Cr, Fe-10.6 Cr, Fe-12.8 Cr and Fe-14.5 Cr) were exposed at 900°C in presence or absence of ash deposit to synthesized flue gas typical of that encountered in fluidized bed coal combustion. The alloys formed a layer of chromium oxide on the surface in the absence of ash deposits. All the alloys tested developed a duplex layer scale in the presence of ash deposits. The outer layer was mainly iron oxide mixed with components of the ash deposit while the inner layer consisted of a mixture of oxide and sulphide of the metals.

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LABORATOIRES DE RECHERCHE EN MÉTALLURGIE PHYSIQUE
RAPPORT ERP/PMRL 82-49(TR)

ÉTUDES SUR LA CORROSION DANS DES MILIEUX SIMULÉS DE COMBUSTION EN LIT FLUIDISÉ. PART I - ENTARTRAGE

par

A.W. Lui*, V.E. Moore** et J.T. McGoey***

RÉSUMÉ

On a exposé quatre aciers inoxydables (types 304, 316, 310 et Uddeholm 904L) et quatre alliages expérimentaux (Fe-8.4 Cr, Fe-10.6 Cr, Fe-12.8 Cr et Fe-14.5 Cr) à une température de 900°C en présence ou en absence de dépôts de cendre afin de synthétiser des gaz de carneau semblable à ceux qui sont produits lors de la combustion en lit fluidisé. Les alliages ont formé une couche d'oxyde de chrome sur la surface de la chaudière en l'absence de dépôt de cendre. Tous les dépôts dont on a fait l'essai on formé une couche double de tartre en présence de dépôts de cendre. La couche externe était constituée principalement d'oxyde de fer mélangé avec des composés des dépôts de cendre, alors que la couche interne était formée d'un mélange d'oxyde et de sulfure des métaux.

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INTRODUCTION

In the fluidized bed combustion (FBC) of coal for power generation, sulphur from the coal is captured by limestone in the bed which reacts with the sulphur dioxide produced by combustion to form calcium sulphate. A problem which has been identified in the use of a sulphur acceptor (limestone) is the induced sulphidation of in-bed heat transfer tubes. Pilot plant tests carried out in the Coal Research Establishment of the U.K. National Coal Board (1), Battelle Laboratory (2) and Oak Ridge National Laboratory (3) have shown that oxidation and sulphidation of FBC heat transfer tubes may occur, particularly in those immersed in the bed.

Recent work on characterizing the bed revealed that in spite of an overall excess air in the combustor and the inherent good mixing characteristic of the fluidized bed, the oxygen potential inside the bed is by no means uniform (4,5). Oxygen probe measurements showed that the partial pressure of oxygen varies from 10^{-14} atm to 10^{-1} atm. When the heat transfer tube is covered with deposits, the oxygen potential at the alloy/deposit interface could be even lower because of oxygen removal by oxidation at the tube at a faster rate than oxygen is resupplied by diffusion through the deposit layer. This is one condition that may initiate sulphidation of in-bed tubes. Pockets of isolated SO_2 gas trapped in the micropores of deposits could produce a relatively high sulphur potential and the $CaSO_4/CaO$ equilibrium could also provide conditions favourable to sulphidation of tubes.

In a fluidized bed combustor, the freeboard conditions governing alloy degradation are relatively simple and not unlike those in other coal combustion systems, but the in-bed conditions are complicated and difficult to simulate in the laboratory. There is an urgent need, at present, for information concerning the corrosion behaviour of heat transfer tubes in fluidized bed combustors. The surface of various alloy steels exposed in the presence or absence of ash deposit to a typical FBC flue gas mixture is characterized in this work.

EXPERIMENTAL

The apparatus used for experiments on samples in the absence of ash deposits is shown in Fig. 1. It consisted essentially of a vertical vycor reactor tube heated by a muffle furnace. The temperature of the furnace was

controlled at 900°C by means of a thermocouple connected to a thermocontroller and was monitored by a digital temperature indicator. Test specimens were suspended, two at a time, inside the reactor tube by means of quartz rods. The "set-up" for metal-gas-deposit corrosion was similar to that described above except that the reactor tube and furnace were in a horizontal position and the test specimens were placed on a ceramic boat. Both faces of the specimen were covered with a simulated ash deposit consisting of 50% $CaSO_4$, 40% CaO and 10% Al_2SiO_4 during these exposure tests. In all cases, the gas mixture flowing at 400 cm^3/min consisted of 2000 ppm SO_2, 2000 ppm CO and 20% CO_2, the balance being nitrogen. The component gases were individually metered by flowmeters, fed into a mixer and analysed with a gas chromatograph before being directed into the reactor tube. The durations of the runs were 1008 hours for metal-gas corrosion and 312 hours for metal-gas-deposit corrosion. At the end of the tests, the reactor tube was flushed with high purity nitrogen and allowed to cool to room temperature before the specimens were removed for examination.

The metal specimens consisted of austenitic steel (types 304, 316, 310 and Uddeholm 904L) and experimental Fe-Cr alloys (Fe-8.4 Cr, Fe-10.6 Cr, Fe-12.8 Cr and Fe-14.54 Cr) and their compositions are shown in Table 1. The alloys were machined to 2.0 x 1.0 x 0.1 cm coupons and ground with 600 grit silicon carbide paper. They were ultrasonically degreased in acetone before being exposed in tests. The exposed specimens were sectioned, mounted and polished for metallographic examination and microprobe analysis. Special care was taken to minimize damage to the surface scale.

RESULTS

Austenitic Steels

Metal-gas corrosion - After 1008 hours exposure to synthesized flue gas at 900°C, the stainless steels all showed similar corrosion morphologies. The scales were thin and adherent. SEM and microprobe analysis showed the scales to be primarily chromium oxide. No sulphur was detected. Figure 2 is typical of SEM micrographs.

Metal-gas-deposit corrosion - After 312 hours exposure to synthesized flue gas while in contact with ash deposit, all stainless steels developed

similar duplex layer scales. In general, the inner layer was porous, consisting of chromium sulphide and nickel sulphide. The outer coarse-grained layer was predominantly iron-oxide containing calcium, aluminum and silicon. The metal substrate in the vicinity of the scale/metal interface was intergranularly attacked and showed a deficiency of chromium. Typical results are shown in Fig. 3, 4 and 5 for type 304 stainless steel.

Experimental Fe-Cr alloys

Metal-gas corrosion - The four Fe-Cr alloys were also exposed to synthesized flue gas for 1008 h at 900°C. The corrosion morphology was similar to that described for the stainless steels. The scale consisted of chromium oxide; sulphur was not detected.

Metal-gas-deposit corrosion - The four Fe-Cr alloys covered with simulated ash deposits were exposed to flue gas for 312 hours. In all cases, duplex layer scales were developed. The inner layer consisted of a small amount of chromium oxide and chromium sulphide intermixed with iron oxide and iron sulphide. The outer layer was mainly iron oxide with calcium, aluminum and silicon uniformly distributed throughout the iron oxide. Typical results are shown in Fig. 6, 7 and 8.

DISCUSSION

In metal-gas corrosion of stainless steels and Fe-Cr alloys, only chromium oxide was detected in the scales examined.

Assuming equlibrium in the gas phase at 900°C for the reaction

$$SO_2 \rightleftharpoons \frac{1}{2} S_2 + O_2 \qquad (1)$$

it can be shown from thermodynamic data of Kubaschewski (6) that

$P_{O2} = 10^{-11}$ atm and

$P_{S2} = 10^{-11}$ atm

In addition, the 100 to 1 ratio of CO_2 to CO in these experiments would yield a P_{O2} of 10^{-12} atm at 900°C and this additional P_{O2} would tend to drive reaction 1 to the left and lower the P_{S2}. As may be seen from Fig. 9, constructed from thermodynamic data in JANAF tables (7), under these conditions, only

oxides of chromium, nickel and iron are stable and sulphides are not expected to form. Chromium oxide (Cr_2O_3) is the expected reaction product under these conditions as has been shown by others (8).

In the metal-gas-deposit reaction, the situation is quite different. At 900°C decomposition of the $CaSO_4$ at the metal surface may occur. Thus, as has been reported by Nauze et al (9)

$$2\ CaSO_4 \rightleftharpoons 2\ CaO + S_2 + 3\ O_2$$

yielding $P_{O2} = 10^{-12}$ atm

$P_{S2} = 10^{-5}$ atm

under these conditions NiS, FeO and Cr_2O_3 are the stable phases (Fig. 9). Duplex layer scale is a common feature in all the stainless steels studied with oxide in the outer layer and oxide plus sulphide in the inner layer. It appears that the alloy initially, at least, is partially covered by a protective oxide scale, presumably Cr_2O_3, and that sulphur is transported through the oxide scale leading to the formation of sulphides beneath. The presence of sulphides will enhance iron ion transport towards the outer surface and iron oxide forms. At the same time, sulphur diffuses inward for sulphide formation. As the sulphur is consumed and when its potential drops below the sulphur potential in Fe/FeS equlibrium, the less stable iron sulphide will then decompose to iron and sulphur. The iron thus formed will be further oxidized to form a porous oxide layer and the sulphur released will diffuse further inward and internal sulphidation will occur. The low concentration of sulphur detected in the inner layers makes this explanation less conclusive in the case of the experimental Fe-Cr alloys.

Microprobe analysis of the metal-gas-deposit sample showed that sulphur was not detected in calcium containing regions. This suggests that the $CaSO_4$ from the deposit was completely decomposed and the sulphur released became a source of sulphur for sulphidation of the alloy. It is also noted that the components of the simulated ash deposit (calcium, aluminum and silicon) were found in the oxide scale [Fig. 5(a) and 8(a)]. The mechanism whereby this mixed scale forms is not understood and the effect of this process on corrosion is not clear at this time.

However, this study clearly demonstrates the severity of corrosion of in-bed heat transfer tubes compared with that of tubes in the freeboard. A further study to assess the relative performance of the alloys under simulated FBC conditions is now underway.

CONCLUSIONS

1. In a gas atmosphere similar to that encountered in fluidized bed coal combustion (2000 ppm SO_2, 2000 ppm CO, 20% CO_2 with the balance nitrogen) at 900°C, both the austenitic steels (types 304, 316, 310 and Uddeholm 904L) and the experimental alloys (Fe-8.4 Cr, Fe-10.6 Cr, Fe-12.8 Cr and Fe-14.5 Cr) formed a layer of chromium oxide on the surface. There was no sign of sulphidation after 1008 hours exposure.
2. In the same gas mixture at 900°C, austenitic stainless steel (type 304, 316, 310 and Uddeholm 904L) and experimental alloys (Fe-8.4 Cr, Fe-10.6 Cr, Fe-12.8 Cr and Fe-14.5 Cr) covered with simulated ash deposit (50% $CaSO_4$, 40% CaO and 10% Al_2SiO_4) were oxidized and sulphidized after 312 hours exposure. Duplex layer scales were observed having an outer layer of oxide and an inner layer of oxide plus sulphide.
3. The components of ash deposit (calcium, aluminum and silicon) were distributed throughout the outer oxide scale.

ACKNOWLEDGEMENTS

The research alloys were prepared by the Foundry Section, Physical Metallurgy Research Laboratories, CANMET.

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Table 1. Composition of alloys (wt %)

	C	Si	Mn	P	S	Ni	Cr	Mo	Cu
Type 304	0.07	0.56	1.14	0.032	0.010	8.76	18.54	-	-
Type 316	0.045	0.52	1.67	0.041	0.002	11.3	16.7	2.6	-
Type 310	0.05	1.02	1.59	0.023	0.008	20.8	24.3	-	-
Uddeholm 904L	0.008	0.56	1.55	0.023	0.001	25.0	19.6	4.63	1.62
Fe-8.4 Cr	0.23	0.40	0.16	0.01	0.01	<0.08	8.4	<0.02	-
Fe-10.6 Cr	0.23	0.41	0.16	0.01	0.01	<0.08	10.6	<0.02	-
Fe-12.8 Cr	0.21	0.40	0.17	0.01	0.01	<0.08	12.8	<0.02	-
Fe-14.5 Cr	0.21	0.40	0.17	0.015	0.01	<0.08	14.5	<0.02	-

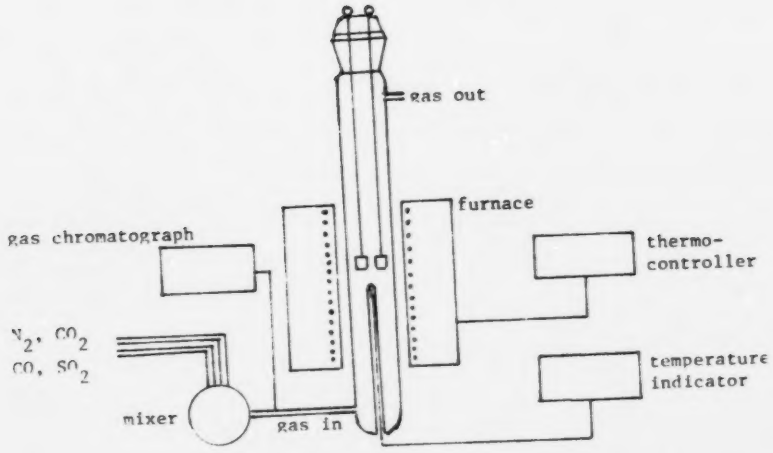

Fig. 1. Schematic diagram of apparatus. (neg 7669)

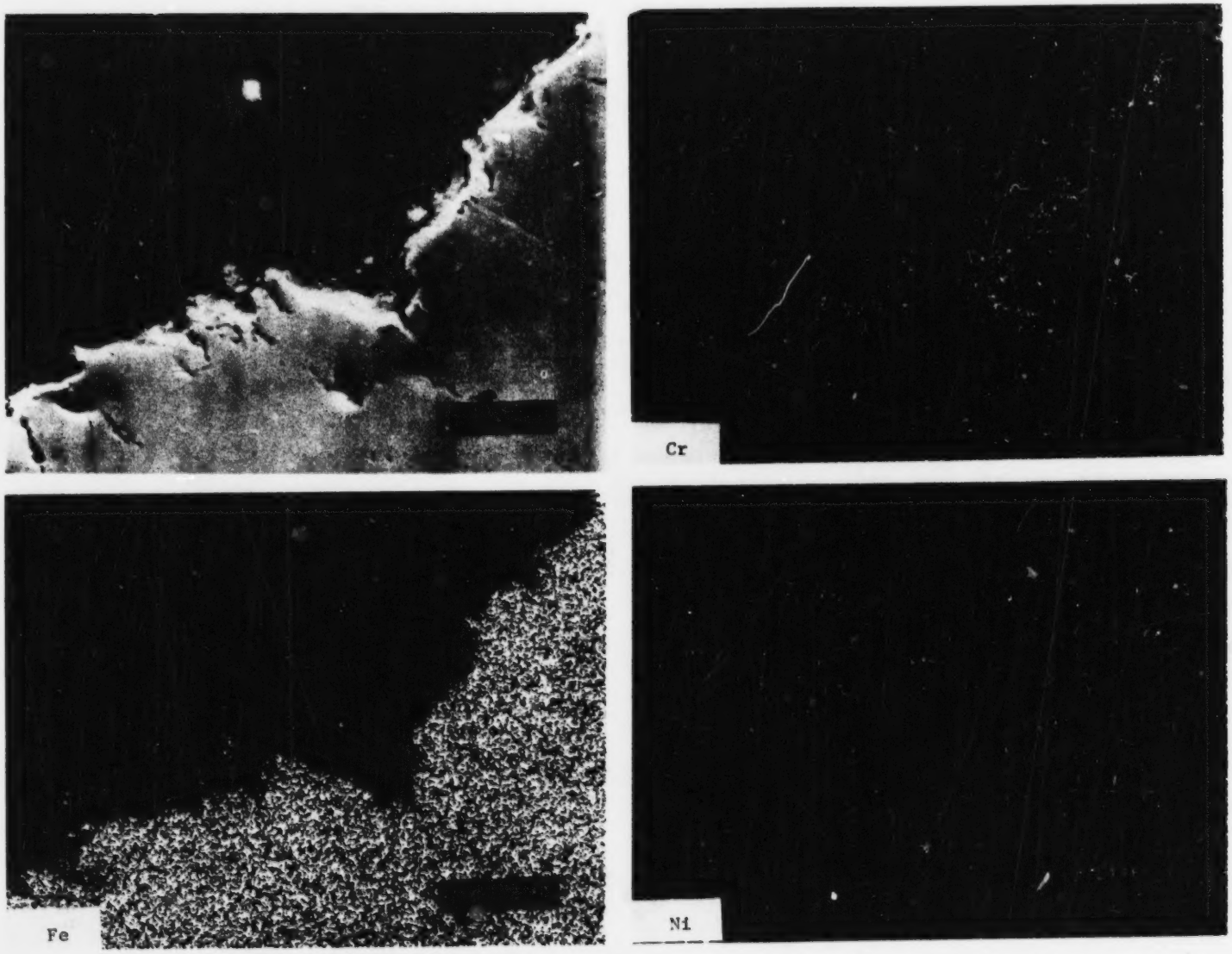

Fig. 2. Electron image of scale on stainless steel type 316, (neg 7670); X-ray micrographs of Fe, (neg 7672); Cr, (neg 7673) and Ni, (neg 7674).

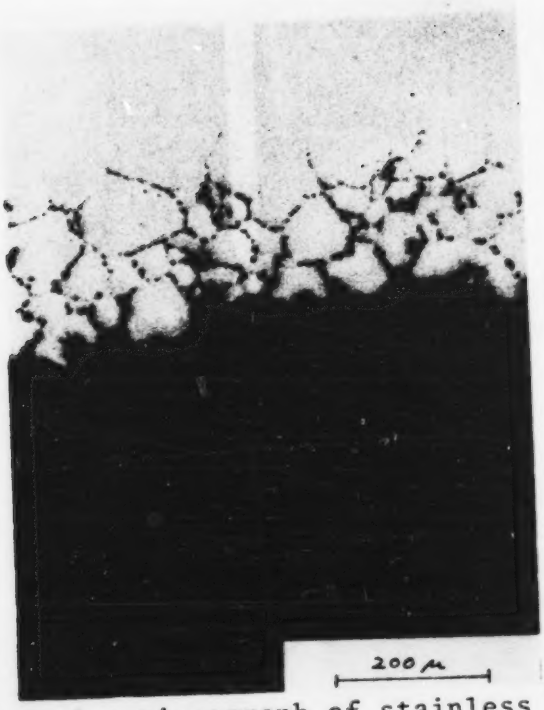

Fig. 3. Cross-section micrograph of stainless steel 304. (neg 7678)

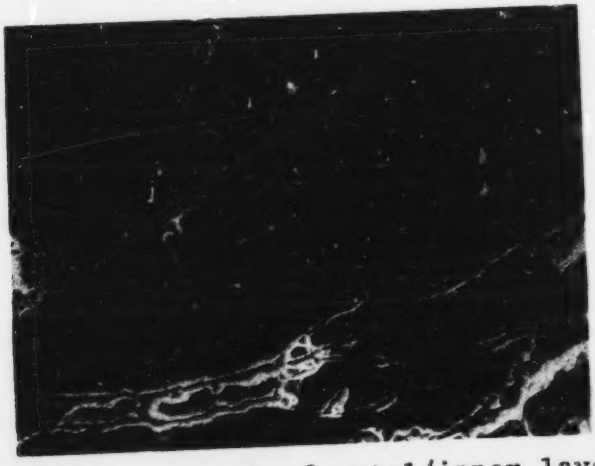

Fig. 4. Electron micrograph of metal/inner layer scale on S.S. 304. X400 (neg 7675)

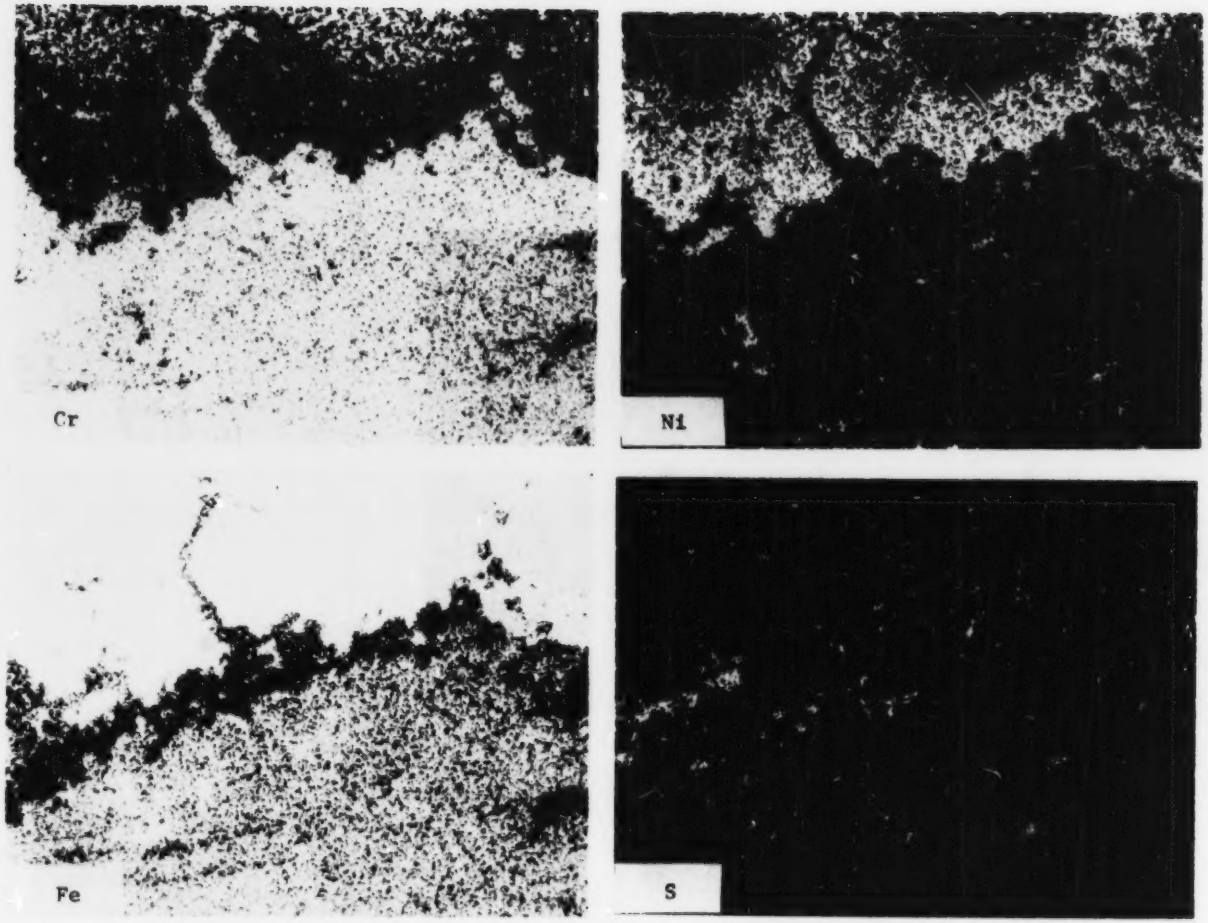

Fig. 4(a). X-ray micrograph of Cr, (neg 7690); Fe, (neg 7691); Ni, (neg 7689); and S (neg 7688) in metal/inner scale.

Fig. 5. Electron micrograph of inner/outer layer scale on S.S. 304. X400. (neg 7687) cont'd.

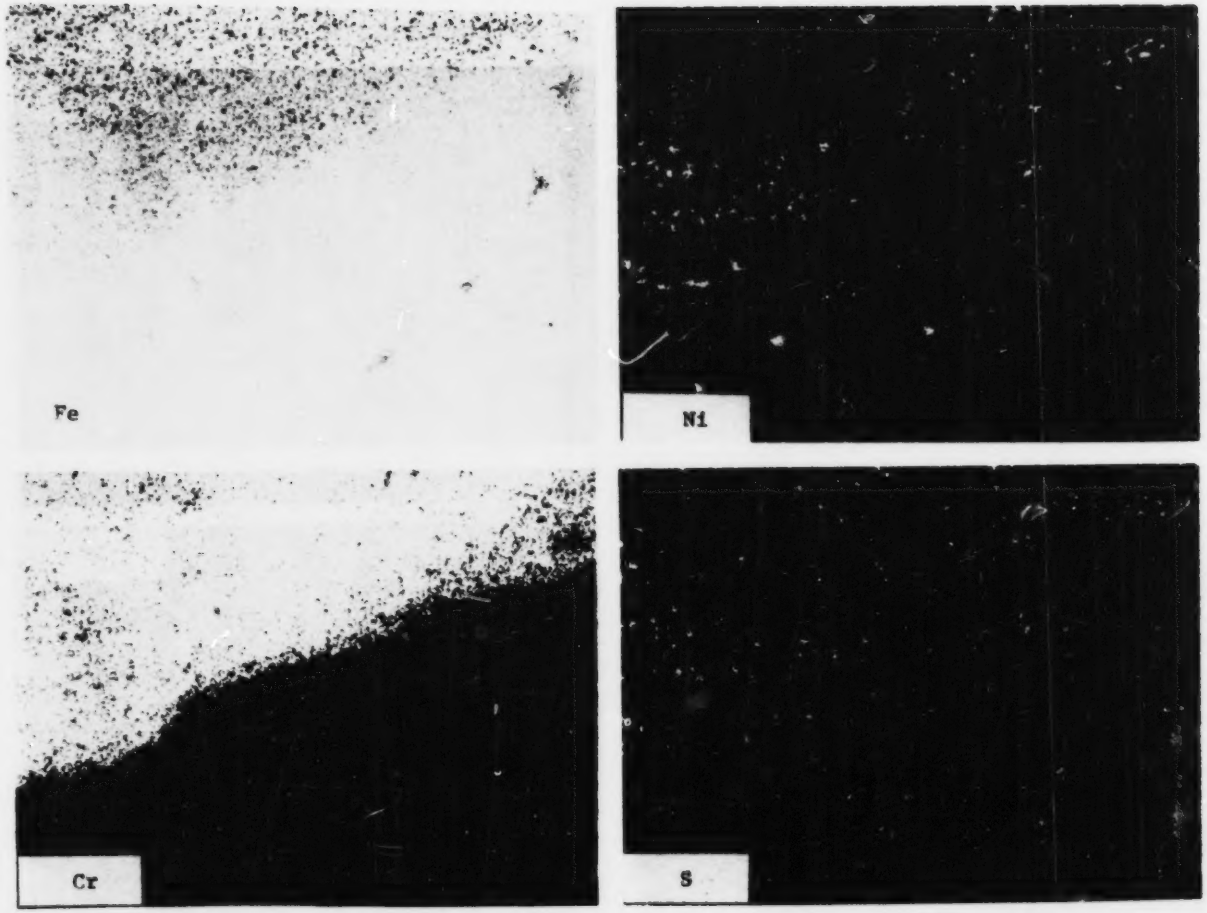

Fig. 5(a). X-ray micrograph of Fe, (neg 7685); Cr, (neg 7684); Ni, (neg 7693); S, (neg 7692) inner/outer scale. (cont'd)

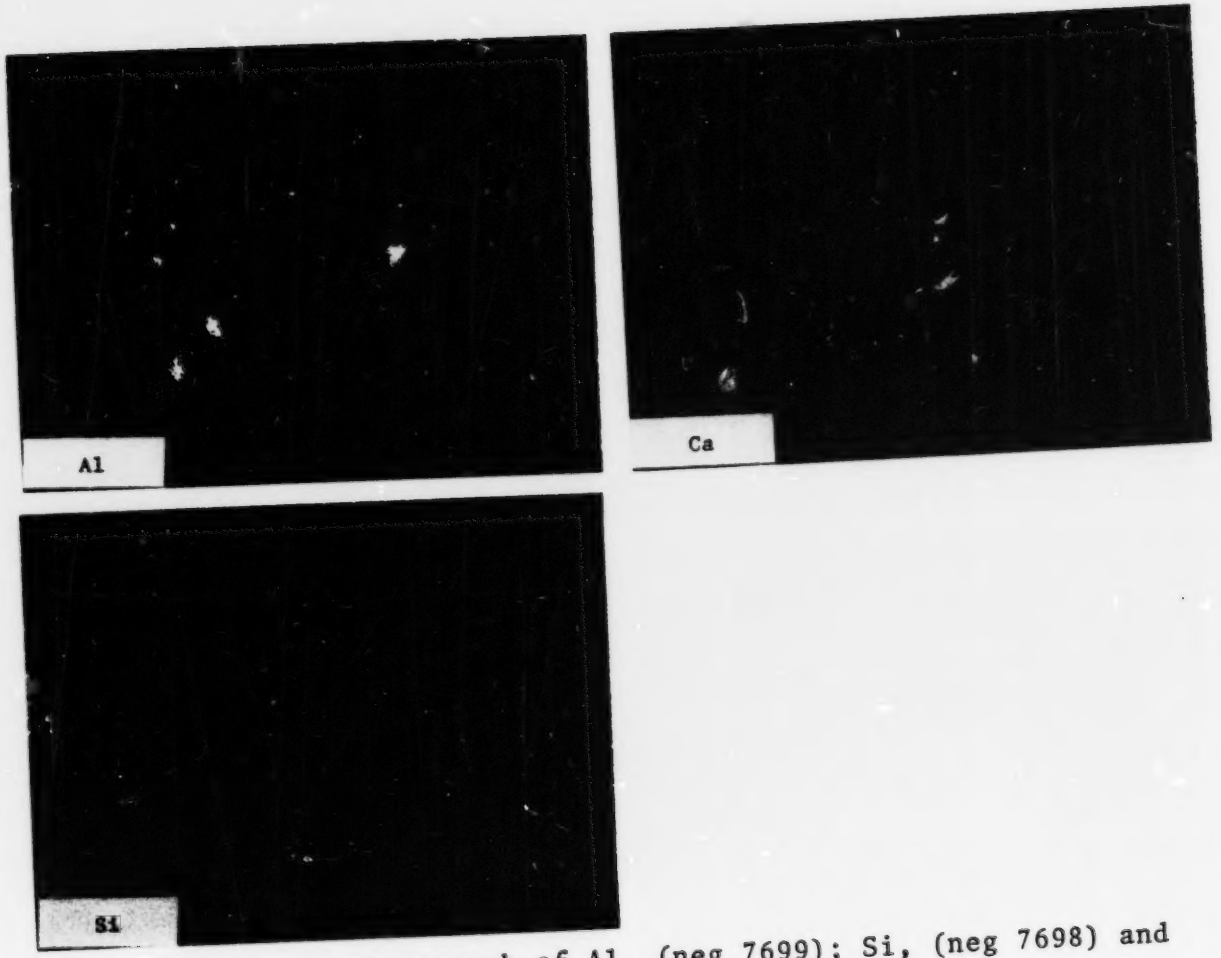

Fig. 5(b) X-ray micrograph of Al, (neg 7699); Si, (neg 7698) and Ca (neg 7686), inner/outer scale.

Fig. 6. Cross-section micrograph of Fe-14.5 Cr alloy. (neg 7676)

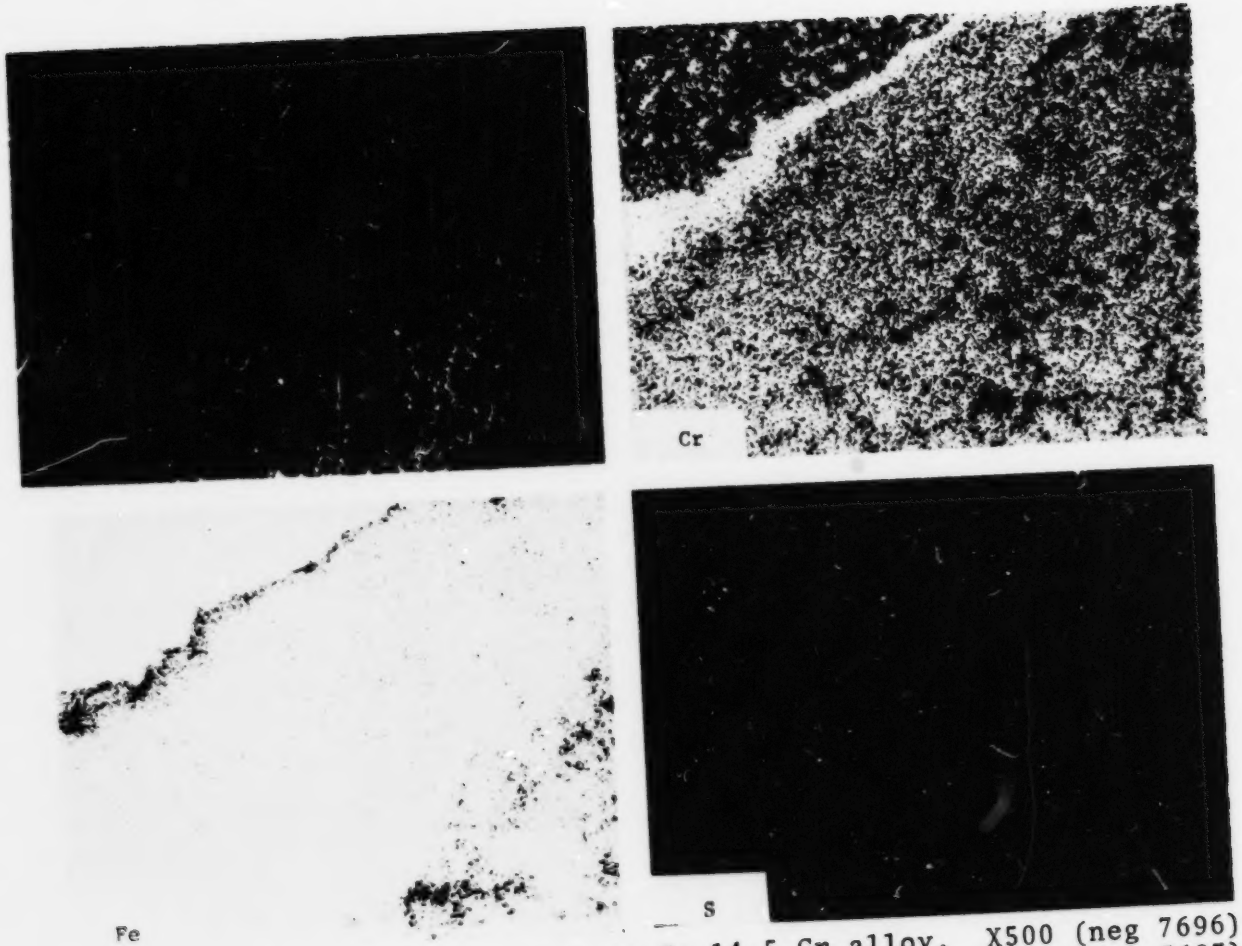

Fig. 7. Electron image of inner scale on Fe 14.5 Cr alloy. X500 (neg 7696) X-ray micrographs of Fe, (neg 7694), Cr (neg 7695) and S (neg 7697) in inner scale.

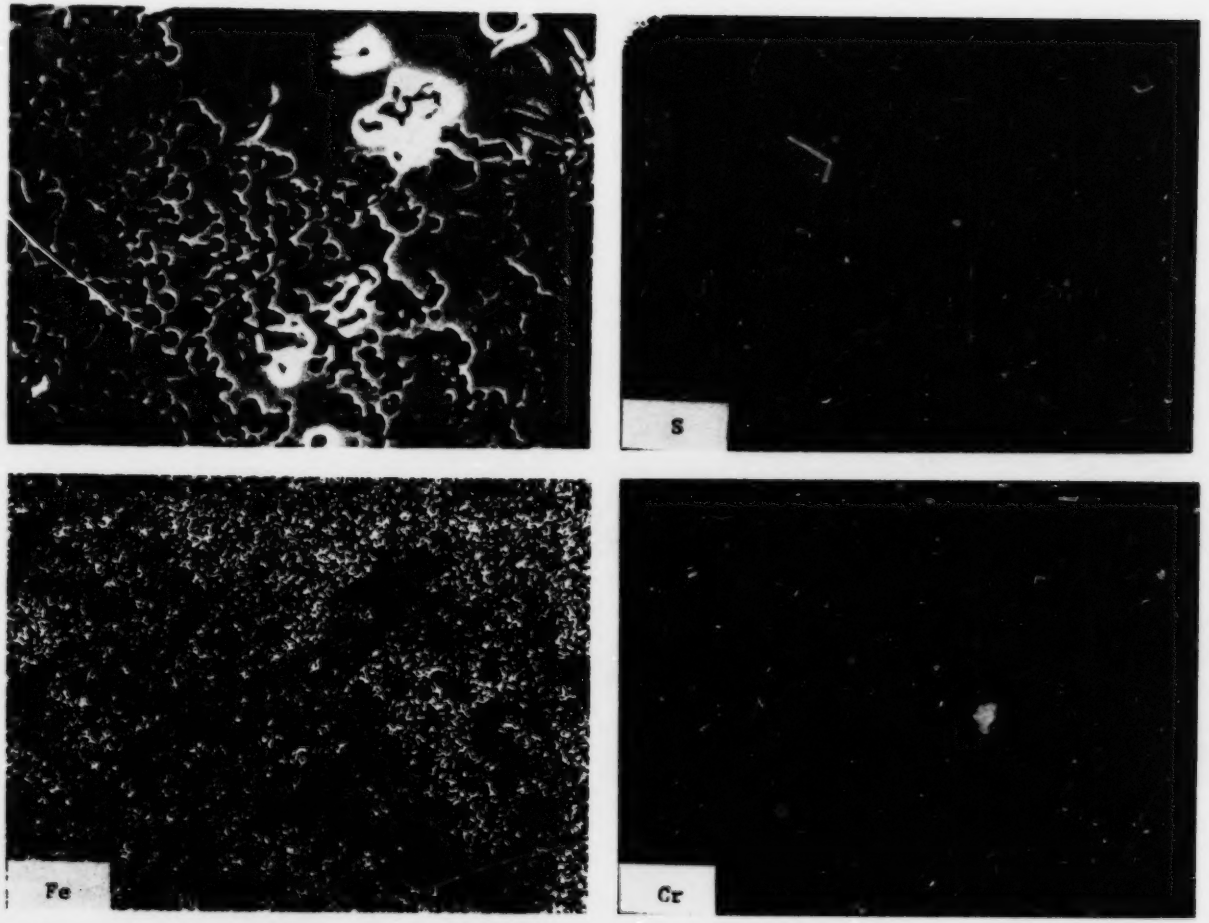

Fig. 8. Electron image of outer scale on Fe 14.5Cr alloy. X800 (neg 7683) X-ray micrographs of Fe, (neg 7682), Cr (neg 7677), S (neg 7681) in outer scale. (cont'd)

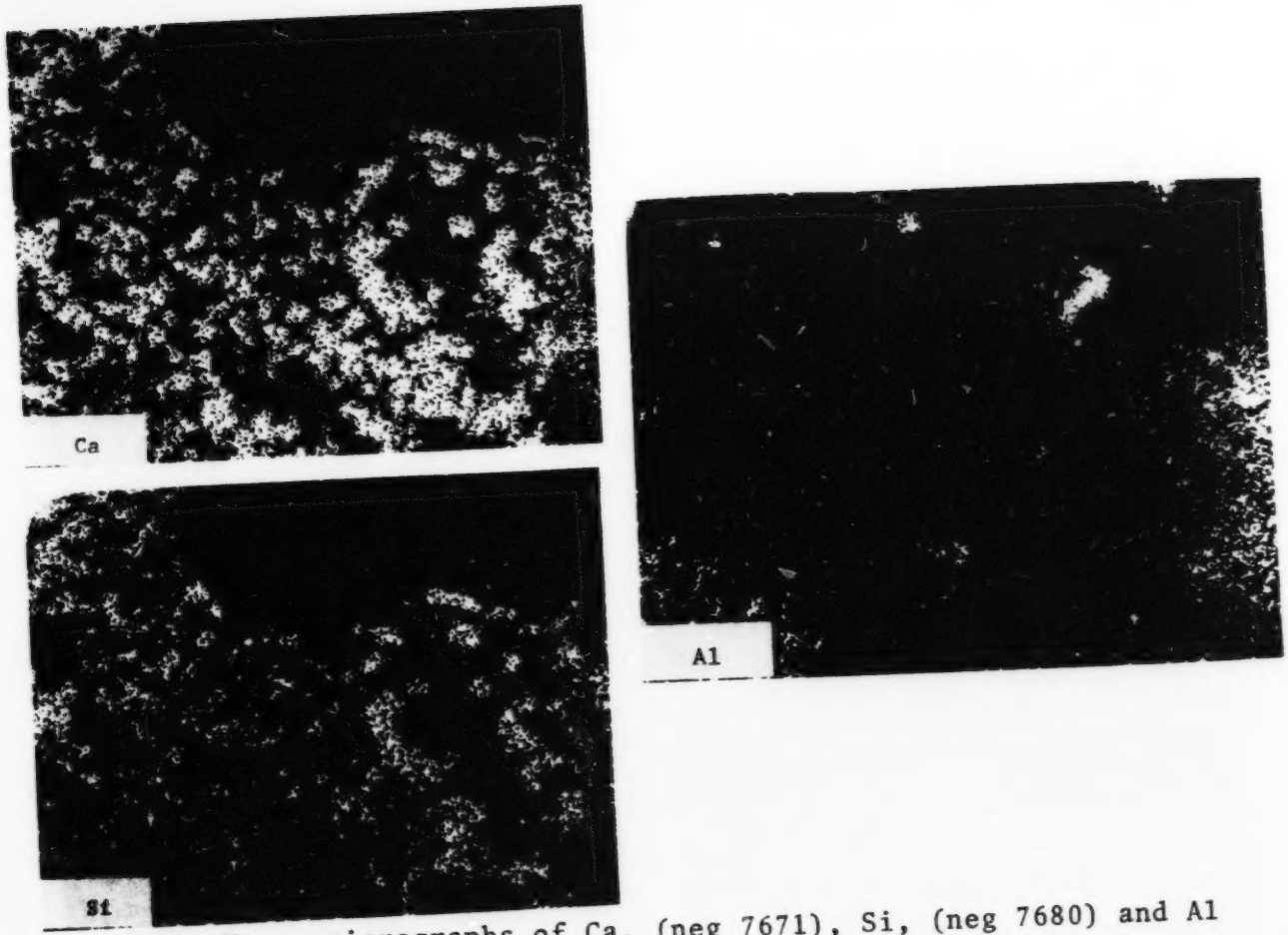

Fig. 8(a). X-ray micrographs of Ca, (neg 7671), Si, (neg 7680) and Al (neg 7679) in outer scale.

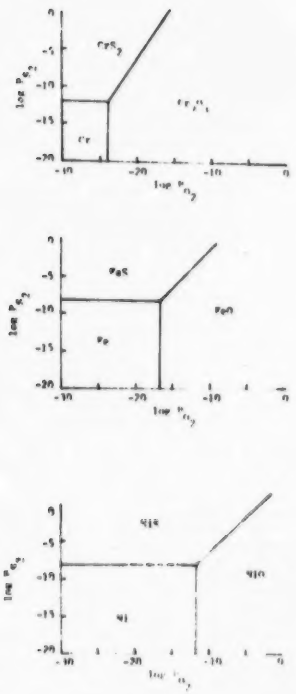

Fig. 9. Phase stability diagrams for systems Cr-O-S and Ni-O-S at 900°C. (neg 7668)